

Chemistry

Lecture 9

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Transition Elements

Outline:

- ✚ General characteristics

Transition Elements

- ◆ The elements which have partially filled d or f orbitals either in atomic state or any of their possible oxidation state
- ◆ They called transition because their properties are transition between s-block and p-block
- ◆ Inner transition elements ⇨ f-block
 - 1st inner transition series [Cerium (Ce) to Lutetium (Lu)] called lanthanides
 - 2nd inner transition series [Thorium (Th) to Lawrencium (Lr)] called actinides
- ◆ Outer transition elements ⇨ d-block
 - 1st outer transition series ⇨ 3d [Scandium (Sc) to Zinc (Zn)]
 - 2nd outer transition series ⇨ 4d [Yttrium (Y) to Cadmium (Cd)]
 - 3rd outer transition series ⇨ 5d [Lanthanum (La) to Mercury (Hg)]
 - 4th outer transition series ⇨ 6d [Actinium (Ac) to onwards] not complete
- ◆ Non-typical ⇨ IIB (Zn, Cd, Hg) and IIIB (Sc, Y, La)
- ◆ Typical ⇨ All others
 - Valence shell configuration of d-block elements ⇨ $(n-1)d^{1-10} s^{1-2}$
 - IB (Cu, Ag, Au) ⇨ Coinage metals
 - 3d-series ⇨ electrons are firstly filled in them

General Features

- They all metallic in nature
- Some of the transition elements play important role in industry i.e. Ti, Cr, Fe, Cu, Mo, W, Zr, Nb, Ta, Th etc
- Hard and strong metals with high M.P and B.P
- Good conductors of heat and electricity
- They form alloys
- With few exception, show variable oxidation state
- Their ions and compounds are coloured in solid and solution state
- Elements and their compounds are used as catalysts
- They form complexes (coordination compounds)
- Tough, malleable and ductile

3d-block elements		4d-block elements		5d-block elements	
Elements	Electronic configuration	Elements	Electronic configuration	Elements	Electronic configuration
Sc (21)	[Ar] 3d ¹ 4s ²	Y (39)	[Kr] 4d ¹ 5s ²	La (57)	[Xe] 5d ¹ 6s ²
Ti (22)	[Ar] 3d ² 4s ²	Zr (40)	[Kr] 4d ² 5s ²	Hf (72)	[Xe] 4f ¹⁴ 5d ² 6s ²
V (23)	[Ar] 3d ³ 4s ²	Nb (41)	[Kr] 4d ⁴ 5s ¹	Ta (73)	[Xe] 4f ¹⁴ 5d ³ 6s ²
Cr (24)	[Ar] 3d ⁵ 4s ¹	Mo (42)	[Kr] 4d ⁵ 5s ¹	W (74)	[Xe] 4f ¹⁴ 5d ⁴ 6s ²
Mn (25)	[Ar] 3d ⁵ 4s ²	Tc (43)	[Kr] 4d ⁵ 5s ²	Re (75)	[Xe] 4f ¹⁴ 5d ⁵ 6s ²
Fe (26)	[Ar] 3d ⁶ 4s ²	Ru (44)	[Kr] 4d ⁷ 5s ¹	Os (76)	[Xe] 4f ¹⁴ 5d ⁶ 6s ²
Co (27)	[Ar] 3d ⁷ 4s ²	Rh (45)	[Kr] 4d ⁸ 5s ¹	Ir (77)	[Xe] 4f ¹⁴ 5d ⁷ 6s ²
Ni (28)	[Ar] 3d ⁸ 4s ²	Pd (46)	[Kr] 4d ¹⁰	Pt (78)	[Xe] 4f ¹⁴ 5d ⁹ 6s ¹
Cu (29)	[Ar] 3d ¹⁰ 4s ¹	Ag (47)	[Kr] 4d ¹⁰ 5s ¹	Au (79)	[Xe] 4f ¹⁴ 5d ¹⁰ 6s ¹
Zn (30)	[Ar] 3d ¹⁰ 4s ²	Cd (48)	[Kr] 4d ¹⁰ 5s ²	Hg (80)	[Xe] 4f ¹⁴ 5d ¹⁰ 6s ²

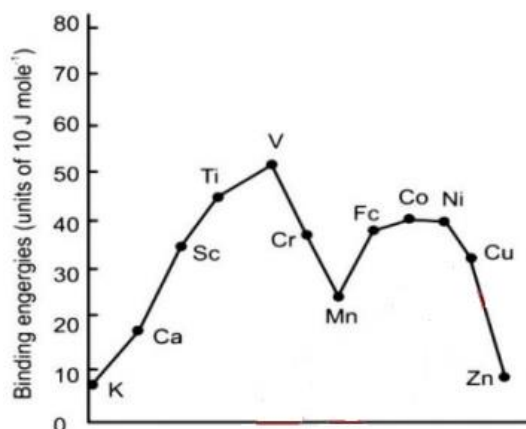
Electronic Structures of 3d

3d-elements	Electronic configuration	es ⁻¹ s-orbital	Electrons in d-orbital d-subshell has total 5 orbital					No. of Unpaired es ⁻¹ in s & d		Oxidation states
₂₁ Sc	₁₈ [Ar], 4s ² , 3d ¹	↓↑	↑					s = 0	d = 1	2, 3
₂₂ Ti	₁₈ [Ar], 4s ² , 3d ²	↓↑	↑	↑				s = 0	d = 2	2, 3, 4
₂₃ V	₁₈ [Ar], 4s ² , 3d ³	↓↑	↑	↑	↑			s = 0	d = 3	2 to 5
₂₄ Cr	₁₈ [Ar], 4s ¹ , 3d ⁵	↑	↑	↑	↑	↑	↑	s = 1	d = 5	2 to 6
₂₅ Mn	₁₈ [Ar], 4s ² , 3d ⁵	↓↑	↑	↑	↑	↑	↑	s = 0	d = 5	1 to 7
₂₆ Fe	₁₈ [Ar], 4s ² , 3d ⁶	↓↑	↓↑	↑	↑	↑	↑	s = 0	d = 4	1 to 6
₂₇ Co	₁₈ [Ar], 4s ² , 3d ⁷	↓↑	↓↑	↓↑	↑	↑	↑	s = 0	d = 3	2 to 5
₂₈ Ni	₁₈ [Ar], 4s ² , 3d ⁸	↓↑	↓↑	↓↑	↓↑	↑	↑	s = 0	d = 2	2 to 4
₂₉ Cu	₁₈ [Ar], 4s ¹ , 3d ¹⁰	↑	↓↑	↓↑	↓↑	↓↑	↓↑	s = 1	d = 0	1 to 3
₃₀ Zn	₁₈ [Ar], 4s ² , 3d ¹⁰	↓↑	↓↑	↓↑	↓↑	↓↑	↓↑	s = 0	d = 0	2

- ☐ Transition elements usually show highest O.S in fluorides and oxides i.e. KMnO₄ (Mn = +7) , CrF₆ (Cr = +6)
- ☐ Oxides in low O.S are basic
- ☐ Oxides in high O.S are acidic

Binding Energy

- Electrons of s-orbital and half filled d-orbitals take part in binding
- Binding energy ∝ No. of unpaired electrons
- Increases across the period due to increase in binding electrons upto V-B and VI-B
- Maximum binding energy is of **V** and minimum is of **Zn**



M.P/B.P

- Directly related to binding forces (binding electrons)
- Increases up to '**V**' and then decreases onwards till '**Zn**' (minimum)
- Highest M.P is of **V** and lowest is of **Zn**
- **Mn** shows abnormality in M.P due to stable configuration (half filled d-subshell) [change in structure]

Covalent Radius and Ionic Radius

- Covalent radii decreases rapidly at the start, then becomes almost constant finally begin to increase at the end of the series
- This is possibly due to increase in shielding effect of 3d-orbitals
- Ionic radii are much less regular

See graph from book to see the change only

Paramagnetism

- ▣ A substance weakly attracted by magnetic field
- ▣ **Paramagnetism:** Due to presence of unpaired electrons
- ▣ **Paramagnetism** \propto **No. of unpaired electrons**
- ▣ Mn^{+2} and Fe^{+3} has maximum unpaired electrons (5 each), have maximum Paramagnetism
- ▣ A substance having no unpaired electron and is weakly repelled by magnetic field is **diamagnetic**
- ▣ The substances which can be magnetized are **ferromagnetic** i.e. Fe, Co, Ni
- ▣ Magnetic moment (μ) = $\sqrt{n(n+2)}$
- ▣ Measured in Bohr magneton (BM) and predicts nature and oxidation state of metal compounds

Oxidation state

- Apparent charge on an atom

- +2 is common O.S (when only electrons of s-orbital are involved)
- Electrons of both 's' and 'd' (unpaired) participate while giving the highest O.S

Color of Transition Metal Complexes

- If all the incident radiation is absorbed, then the substance looks black
- If all the incident radiation is reflected then the substance looks white
- If only a very small proportion of the incident white light is absorbed and if all the radiations in the visible region of spectrum are transmitted equally then the substance will appear colorless
- For color:
 - ☞ Presence of unpaired electrons (incomplete d-subshell)[Main factor]
 - ☞ Nature of ligand (cause splitting of d-orbitals)
- Ligand splits the d-orbitals into two energy levels
- 2 of higher and 3 of lower energy
- Electrons residing in lower energy level absorb part of visible light and jumps to higher energy level (called **d-d transition**)
- Every ion absorbs different wavelength while transmits other (gives color)
- $[\text{Ti}(\text{H}_2\text{O})_6]^{+3}$ absorbs yellow light and transmits blue + red = violet
- Complementary color scheme:
 - ☞ **Red \Leftrightarrow Green**
 - ☞ **Blue \Leftrightarrow Orange**
 - ☞ **Yellow \Leftrightarrow Violet**

Interstitial Compounds

- Small non metals i.e. H, B, C, N fill the interstices of transition elements
- Impart useful features to metal
- These are non-stoichiometric compounds
- Also termed as interstitial alloys

Alloy Formation

- Homogeneous mixture of two or more than metals forming substitutional alloy
- Owing to similar size, some transition metal atoms are able to replace one another
- **Properties**
 - ✓ Alloys are comparatively cheap
 - ✓ Strong and flexible but hard alloys can be prepared
 - ✓ Don't corrode (long life)
 - ✓ High M.P, better conductors but non-conductor alloys can also be prepared
- **Examples** Steel (iron atoms are substituted by Cr, Mn and Ni)

Alloys of Metals	Composition	Properties and Uses
Brass	Cu = 60 – 80 % Zn = 20 – 40 %	It is a strong alloy of copper which is soft and flexible. It does not corrode. Due to low melting point, it is easy to use. It is used to make locks, keys, water taps, pipes, artificial jewellery, door handles and parts of machines
Bronze	Cu 90 - 95 % Sn 5 - 10 %	It is strong, brilliant and long lasting. It does not corrode. It is used to prepare medals, coins, badges and bullets etc. besides these; decorative articles are also made from this alloy.
Nichrome	Ni = 60 % Cr = 15 % Fe = 25 %	It is used in electric heaters and filaments of furnaces.

Uses as a Catalyst

Transition elements and their compounds are catalyst due to;

- ❖ Presence of partially or vacant d-orbitals
- ❖ Defects in crystal lattices
- ❖ Exhibit variable O.S
- ❖ Form reaction intermediates
- ❖ Form interstitial compounds which can absorb an activator to reacting species

Some Examples:

- **Fe** in Haber process of ammonia synthesis
- **Ni, Pt, Pd** in Hydrogenation
- **MnO₂** for decomposition of H₂O₂
- **Cu** in preparation of benzene from acetylene and oxidation of alkanes (synthesis of fatty acids)
- **Zn** in reduction of alkyl halides to alkanes, vicinal dihalides to alkenes, in ozonolysis for reduction of H₂O₂ to water and phenol to benzene
- **FeX₃** in halogenation of aromatic compounds
- **ZnCl₂** in preparation of alkyl halides from alcohols
- **ZnO + Cr₂O₃** in prep. of methanol from water gas
- **TiCl₄ + Al(C₂H₅)₃** better quality of polythene
- **V₂O₅/Pt** in contact process
- **Mo** is also sometimes used as a promoter

Formation of Complexes

- Due to small size of metal cation
- Due to high charge of metal cation
- Due to availability of vacant d-orbital

Central Metal Atom:

- Atom to which ligands are attached

- Fe is central metal atom in $K_4[Fe(CN)_6]$

Ligands:

- Species attached to central metal atom and donating electron pair to metal
- CN is ligand in $K_4[Fe(CN)_6]$ and are 6 in strength
- **Neutral Ligands:** NH_3 (amine), H_2O (aqua), CO (carbonyl), N_2H_4 (hydrazine)
- **Negative Ligands:** CN^{-1} (cyano), Cl^{-1} (chloro), F^{-1} (fluoro), NO_2^{-1} (nitro), OH^{-1} (hydroxo), CO_3^{-2} (carbonato), CH_3COO^{-1} (acetato), $^{1-}OOC-COO^{-1}$ (oxalato) [ending name with 'O']
- **Positive Ligands:** $NH_2NH_3^+$ (Hydrazinium), NO^+ (Nitrosonium)
- **Monodentate Ligands:** Only donating one electron pair to metal i.e. NH_3 , H_2O , CN^{-1} , Cl^{-1} , NO_2^{-1} , OH^{-1} etc
- **Bidentate Ligands:** Donate two electron pairs to metal i.e. N_2H_4 , CO_3^{-2} , $^{1-}OOC-COO^{-1}$
- **Polydentate Ligands:** EDTA (Ethylenediaminetetraacetate ion)

Coordination Sphere: Square brackets containing both metal atom and ligands.

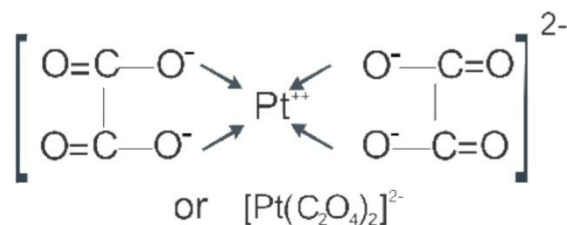
Charge on Coordination Sphere: Charge present on metal ion + total charge on the ligands i.e. in $K_4[Fe(CN)_6]$, charge on coordination sphere = -4

Coordination Number: Total no. of electron pairs donated by ligands to metal atom i.e. in $K_4[Fe(CN)_6]$, coordination number = 6

- ☞ Most common coordination number in the complex compounds is 6 (most common geometry is octahedral)

Chelate:

- All the donor atoms of polydentate ligand get coordinated with metal ion, a complex is formed consisting of one or more rings called chelate
- Two 5-membered rings
- Coordination no. = 4



Dioxalato- platinate (II)ion

Nomenclature:

- Name of cation followed by anion
- Name of Coordination sphere (can be cation or anion):
 - Name of ligand + name of metal
 - Different ligands are named alphabetically regardless of their nature
 - If same ligand, use prefixes di, tri, tetra etc
 - Metal name ends with "ate"(suffix) if charge on coordination sphere is negative otherwise remains same
 - Name of metal is followed by its O.S written in Roman numerals
- For example $K_4[Fe(CN)_6]$ ☞ Potassium hexacyano ferrate (II)

- In writing the formula, [metal + negative ligands (alphabetically) + neutral ligands (alphabetically)]

Geometry and Isomerism of Complex ions with Coordination Number 4 and 6

Geometry:

- ▣ Common geometry is octahedral
- ▣ Factors affecting geometry:
 - ☞ No. of electron pairs donated by ligands
 - ☞ Hybridization state of metal
 - ☞ Nature of ligand

No. of e ⁻ pairs	Hybridization	Geometry
2	sp	Linear
3	sp ²	Triangular
4	sp ³	Tetrahedral
	dsp ²	Square planner
5	dsp ³ /sp ³ d	Trigonal bipyramidal
6	d ² sp ³ /sp ³ d ²	Octahedral

- ▣ Square planner is usually when; (short cut)
 - Strong ligand is present (CO, CN⁻, NH₃, ethylene diammine) or
 - d⁸ electronic configuration i.e. Rh⁺¹, Pd⁺², Pt⁺², Au⁺³, Ni⁺² etc
- ▣ **Examples:** [MnCl₄]⁻² is tetrahedral (sp³), {[Cu(NH₃)₄]⁺², [Pt(NH₃)₄]⁺², [AuCl₄]⁻¹} are square planner (dsp²), [PCl₅] is bipyramidal (dsp³), [Co(NH₃)₆]⁺³ is octahedral (sp³d²)